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Composition for coating keratin fibres with a high dry extract comprising a block polymer

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The subject of the present invention is a cosmetic composition for coating keratin fibres comprising a block polymer.

The invention also relates to a cosmetic process for making up or treating keratin fibres such as the eyelashes, the eyebrows and the hair.

The composition according to the invention may be a makeup composition, also called mascara, a makeup base for keratin fibres or base coat, a composition to be applied over makeup, also known as top coat, or a composition for treating keratin fibres. More especially, the composition according to the invention is a mascara.

The term "mascara" is understood as meaning a composition intended to be applied to the eyelashes: it may be a makeup composition for the eyelashes, a makeup base for the eyelashes, a composition to be applied over a mascara, also known as top coat, or a cosmetic treatment composition for the eyelashes. The mascara is more particularly intended for the eyelashes of human beings, but also for false eyelashes.

Preferably, the composition according to the invention is a leave-in composition.

Makeup compositions for the eyes, and in particular for the eyelashes, such as mascaras, may be provided in various forms: for example in the form of biphasic oil-in-water or O/W or water-in-oil W/O

emulsions, or of aqueous or anhydrous dispersions.

It is generally through the qualitative and quantitative choice of the waxes and polymers that the desired specificities of application are adjusted for the makeup compositions, such as their fluidity, their covering power and/or their curling power. Thus, it is possible to prepare various compositions which, when applied in particular to the eyelashes, induce varied effects of the lengthening, curling and/or thickening type (charging or volumizing effect).

It is known from the prior art that the higher the content of solids (provided in part by a fatty phase consisting, for example, of one or more waxes or of one or more lipophilic polymers) in a composition, the greater the deposition of material on the eyelashes and therefore the more the result obtained will be volumizing.

However, the increase in the content of solids in a composition, such as an emulsion or dispersion, causes an increase in the consistency of the product obtained and therefore a delicate and difficult application to the eyelashes because the product is thick and viscous, it forms a deposit with difficulty, in a heterogeneous manner and in packets. The increase in the content of solids is therefore often limited by the increase in consistency and does not exceed 45% of the total weight of the composition.

This limitation on the content of solids is often linked to the impossibility of increasing, on the one hand, the wax content in the fatty phase which does not exceed 25% for reasons of feasibility (the compositions comprising between 20 and 25% by weight of wax are often very thick, compact, difficult to apply and have unsatisfactory cosmetic properties) and, on the other hand, of incorporating fat-soluble polymers in a large amount, which considerably increases the viscosity of the composition.

Another means of increasing the content of solids is to incorporate solid particles such as fillers or pigments, but the increase in consistency also limits the maximum percentage of solids. Furthermore, the use of solid particles in a large quantity does not promote homogeneous and smooth deposition not only because of the consistency but also because of the size of the particles introduced, which gives a granular and unsmooth appearance to the deposit.

That is generally the case for the so-called volumizing mascaras which are difficult to apply and which give a heterogeneous makeup.

It is therefore difficult to obtain a makeup composition for the keratin fibres, comprising a high content of solids and therefore a satisfactory volumizing effect, which has easy and homogeneous

application.

Moreover, the increase in the content of solids and the nonhomogeneity of the deposit causes a poorer staying power of the composition film: the latter is not sufficiently resistant to rubbing, in particular of the fingers, and/or to water, during bathings and/or showers for example, or alternatively to tears or to sweat. The mascara then tends to crumble over time: grains become deposited and leave marks around the eye.

The aim of the present invention is therefore to propose another route for formulating a composition for coating the keratin fibres leading to a keratin fibre charging effect, and which completely or partially solves the problems linked to conventional routes of formulation. In addition, the compositions according to the invention allow smooth and homogeneous application and lead to a makeup for keratin fibres exhibiting good staying power.

The inventors have discovered that a composition of this type could be obtained using a particular block polymer. Surprisingly, the incorporation of such a polymer at high or very high contents (which may be up to 50% by weight) makes it possible to significantly increase the dry matter content of a composition for coating keratin fibres, while preserving a consistency which allows easy

application to the keratin fibres, and leads, after application to keratin fibres, to a makeup film with good staying power over time: the film does not crumble.

More precisely, a subject of the invention is a composition for coating keratin fibres comprising, in a cosmetically acceptable organic liquid medium, a film-forming linear ethylenic block polymer, called in the text that follows "block polymer", the said composition having a dry matter or dry extract content greater than or equal to 45% by weight.

A subject of the invention is also a cosmetic process for making up or for the nontherapeutic care of keratin fibres, in particular the eyelashes, comprising the application of a composition as defined above to the keratin fibres.

A subject of the invention is also the use of a composition as defined above for obtaining a makeup for the keratin fibres, in particular the eyelashes, which is charging and/or has good staying power.

A subject of the invention is also the use of a film-forming linear ethylenic block polymer in a composition for coating keratin fibres, in order to obtain a composition that is easy to apply to the keratin fibres and/or leading to a makeup which is charging and/or has good staying power on the said keratin fibres.

The term "cosmetically acceptable" organic liquid medium means an organic liquid medium that is compatible with the eyelashes or the skin.

Protocol for measuring the dry matter or dry extract content

The dry matter content, that is to say the content of nonvolatile material, may be measured in different ways; mention may be made for example of the methods based on drying in an oven, the methods based on exposure to infrared radiation and the chemical methods based on titration of water according to Karl Fischer.

Preferably, the dry extract of the compositions according to the invention is measured on a Mettler Toledo HG 53 balance (Halogen Moisture Analyzer).

A mascara sample (2-3 g) is deposited in an aluminium dish and subjected to a temperature of 120°C for 60 minutes. The measurement of the dry extract corresponds to the monitoring of the mass of the sample as a function of time. The final content of solids is therefore the percentage of the final mass (at the end of 60 min) relative to the initial mass: DE = (final mass/initial mass) × 100.

The composition according to the invention has a dry matter content greater than or equal to 45%, preferably greater than 46%, even better greater than

or equal to 47%, better still greater than 48%, preferably still greater than or equal to 50%, and may be up to 70%.

1) Block polymer

The polymer of the composition according to the invention is a film-forming linear ethylenic block polymer.

The term "ethylenic" polymer means a polymer obtained by polymerizing monomers comprising an ethylenic unsaturation.

The term "block" polymer means a polymer comprising at least 2 different blocks, preferably at least 3 different blocks.

The polymer is a polymer with a linear structure. In contrast, a polymer of non-linear structure is, for example, a polymer of branched, starburst or grafted structure, or the like.

The term "film-forming" polymer means a polymer capable of forming, by itself or in the presence of an auxiliary film-forming agent, a continuous film that adheres to a support and especially to keratin materials.

Advantageously, the block polymer of the composition according to the invention is free of styrene. The term "polymer free of styrene" means a polymer containing less that 10% by weight, relative to the total weight of the polymer, preferably less than

5% by weight, even better less than 2% by weight, even better less than 1% by weight, or not even containing none of a styrene monomer such as styrene, styrene derivatives such as methylstyrene, chlorostyrene or chloromethylstyrene of styrene or of styrene derivatives such as for example methylstyrene, chlorostyrene or chloromethylstyrene.

According to one embodiment, the block polymer of the inventive composition is derived from aliphatic ethylenic monomers. The term "aliphatic monomer" means a monomer comprising no aromatic groups.

According to one embodiment, the block polymer is an ethylenic polymer derived from aliphatic ethylenic monomers comprising a carbon-carbon double bond and at least one ester group -COO- or amide group -CON-. The ester group may be linked to one of the two unsaturated carbons via the carbon atom or the oxygen atom. The amide group may be linked to one of the two unsaturated carbons via the carbon atom or the nitrogen atom.

Preferably, the block polymer of the composition according to the invention comprises at least one first block and at least one second block having different glass transition temperatures (Tg), the said first and second blocks being linked together via an intermediate block comprising at least one constituent monomer of the first block and at least one

constituent monomer of the second block.

The term "at least one" block means one or more blocks.

It is pointed out that, in the text hereinabove and hereinbelow, the terms "first" and "second" blocks do not in any way condition the order of the said blocks in the polymer structure.

Advantageously, the first and second blocks of the block polymer are mutually incompatible.

The term "mutually incompatible blocks" means that the mixture formed from the polymer corresponding to the first block and from the polymer corresponding to the second block is not miscible in the organic liquid medium that is contained in major amount by weight in the organic liquid medium of the composition, at room temperature (25°C) and atmospheric pressure (10^5 Pa), for a content of the polymer mixture of greater than or equal to 5% by weight, relative to the total weight of the mixture (polymers and solvent), it being understood that:

i) the said polymers are present in the mixture in a content such that the respective weight ratio ranges from 10/90 to 90/10, and

ii) each of the polymers corresponding to the first and second blocks has an average (weight-average or number-average) molecular mass equal to that of the block polymer ± 15%.

When the organic liquid medium comprises a mixture of organic liquids, in the case of two or more liquids present in identical mass proportions, the said polymer mixture is immiscible in at least one of them.

Obviously, when the organic liquid medium comprises only one organic liquid, the latter is the major organic liquid.

Advantageously, the major organic liquid of the composition is the organic solvent for polymerizing the block polymer or the major organic solvent of the mixture of organic solvents for polymerizing the block polymer. The intermediate block is a block comprising at least one constituent monomer of the first block and at least one constituent monomer of the second block of the polymer makes it possible to "compatibilize" these blocks.

Preferably, the block polymer comprises no silicon atoms in its skeleton. The term "skeleton" means the main chain of the polymer, as opposed to the pendant side chains.

Preferably, the block polymer is not water-soluble, i.e. the polymer is not soluble in water or in a mixture of water and linear or branched lower monoalcohols containing from 2 to 5 carbon atoms, for instance ethanol, isopropanol or n-propanol, without pH modification, at an active material content of at least 1% by weight, at room temperature (25°C).

Preferably, the polymer according to the invention is not an elastomer.

The term "non-elastomeric polymer" means a polymer which, when it is subjected to a constraint intended to stretch it (for example by 30% relative to its initial length), does not return to a length substantially identical to its initial length when the constraint ceases.

More specifically, the term "non-elastomeric polymer" denotes a polymer with an instantaneous recovery $R_i < 50\%$ and a delayed recovery $R_{2h} < 70\%$ after having been subjected to a 30% elongation. Preferably, R_i is $< 30\%$ and $R_{2h} < 50\%$.

More specifically, the non-elastomeric nature of the polymer is determined according to the following protocol:

A polymer film is prepared by pouring a solution of the polymer into a Teflon-coated mould, followed by drying for 7 days in an environment conditioned at 23 ± 5°C and 50 ± 10% relative humidity.

A film about 100 μm thick is thus obtained, from which are cut rectangular specimens (for example using a punch) 15 mm wide and 80 mm long.

This sample is subjected to a tensile stress using a machine sold under the reference Zwick, under the same temperature and humidity conditions as for the drying.

The specimens are pulled at a speed of 50 mm/min and the distance between the jaws is 50 mm, which corresponds to the initial length (l_0) of the specimen.

The instantaneous recovery R_i is determined in the following manner:

- the specimen is pulled by 30% (ε_{max}), i.e. about 0.3 times its initial length (l_0)
- the constraint is released by applying a return speed equal to the tensile speed, i.e. 50 mm/min, and the residual elongation of the specimen is measured as a percentage, after returning to zero constraint (ε_i).

The percentage instantaneous recovery (R_i) is given by the following formula:

$$R_i = (\varepsilon_{max} - \varepsilon_i)/\varepsilon_{max}) \times 100$$

To determine the delayed recovery, the percentage residual elongation of the specimen (ε_{2h}) is measured, 2 hours after returning to zero constraint.

The percentage delayed recovery (R_{2h}) is given by the following formula:

$$R_{2h} = (\varepsilon_{max} - \varepsilon_{2h})/\varepsilon_{max}) \times 100$$

Purely as a guide, a polymer according to one embodiment of the invention has an instantaneous recovery R_i of 10% and a delayed recovery R_{2h} of 30%.

Advantageously, the block polymer used in the composition according to the invention has a

polydispersity index I of greater than 2, for example ranging from 2 to 9, preferably greater than or equal to 2.5, for example ranging from 2.5 to 8 and better still greater than or equal to 2.8, and especially ranging from 2.8 to 6.

The polydispersity index I of the block polymer is equal to the ratio of the weight-average mass Mw to the number-average mass Mn.

The weight-average molar mass (Mw) and number-average molar mass (Mn) are determined by gel permeation liquid chromatography (THF solvent, calibration curve established with linear polystyrene standards, refractometric detector).

The weight-average mass (Mw) of the block polymer is preferably less than or equal to 300 000; it ranges, for example, from 35 000 to 200 000 and better still from 45 000 to 150 000.

The number-average mass (Mn) of the block polymer is preferably less than or equal to 70 000; it ranges, for example, from 10 000 to 60 000 and better still from 12 000 to 50 000.

Each block of the block polymer of the composition according to the invention is derived from one type of monomer or from several different types of monomer.

This means that each block may consist of a homopolymer or a copolymer; this copolymer constituting

the block may in turn be random or alternating.

Advantageously, the intermediate block comprising at least one constituent monomer of the first block and at least one constituent monomer of the second block of the polymer is a random polymer.

Preferably, the intermediate block is derived essentially from constituent monomers of the first block and of the second block.

The term "essentially" means at least 85%, preferably at least 90%, better still 95% and even better still 100%.

Advantageously, the intermediate block has a glass transition temperature Tg of between the glass transition temperatures of the first and second blocks.

The glass transition temperatures indicated for the first and second blocks may be theoretical Tg values determined from the theoretical Tg values of the constituent monomers of each of the blocks, which may be found in a reference manual such as the Polymer Handbook, 3rd Edition, 1989, John Wiley, according to the following relationship, known as Fox's law:

$$1/Tg=\sum_i (\varpi_i/Tg_i),$$

ϖ_i being the mass fraction of the monomer i in the block under consideration and Tg_i being the glass transition temperature of the homopolymer of the monomer i.

Unless otherwise indicated, the Tg values

indicated for the first and second blocks in the present patent application are theoretical Tg values.

The difference between the glass transition temperatures of the first and second blocks is generally greater than 10°C, preferably greater than 20°C and better still greater than 30°C.

In particular, the first block may be chosen from:

- a) a block with a Tg of greater than or equal to 40°C,

- b) a block with a Tg of less than or equal to 20°C,

- c) a block with a Tg of between 20 and 40°C,

and the second block can be chosen from a category a), b) or c) different from the first block.

In the present invention, the expression: "between ... and ..." is intended to denote a range of values for which the limits mentioned are excluded, and "from ... to ..." and "ranging from ... to ..." are intended to denote a range of values for which the limits are included.

<u>a) Block with a Tg of greater than or equal to 40°C</u>

The block with a Tg of greater than or equal to 40°C has, for example, a Tg ranging from 40 to 150°C, preferably greater than or equal to 50°C, for example ranging from 50°C to 120°C and better still

greater than or equal to 60°C, for example ranging from 60°C to 120°C.

The block with a Tg of greater than or equal to 40°C may be a homopolymer or a copolymer.

In the case where this block is a homopolymer, it is derived from monomers which are such that the homopolymers prepared from these monomers have glass transition temperatures of greater than or equal to 40°C. This first block may be a homopolymer consisting of only one type of monomer (for which the Tg of the corresponding homopolymer is greater than or equal to 40°C).

In the case where the first block is a copolymer, it may be totally or partially derived from one or more monomers, the nature and concentration of which are chosen such that the Tg of the resulting copolymer is greater than or equal to 40°C. The copolymer may comprise, for example:

- monomers which are such that the homopolymers prepared from these monomers have Tg values of greater than or equal to 40°C, for example a Tg ranging from 40 to 150°C, preferably greater than or equal to 50°C, for example ranging from 50°C to 120°C and better still greater than or equal to 60°C, for example ranging from 60°C to 120°C, and

- monomers which are such that the homopolymers prepared from these monomers have Tg

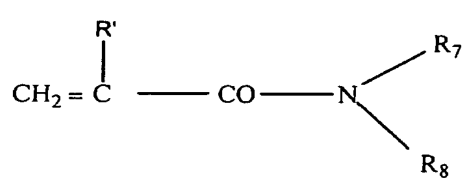
values of less than 40°C, chosen from monomers with a Tg of between 20 and 40°C and/or monomers with a Tg of less than or equal to 20°C, for example a Tg ranging from -100 to 20°C, preferably less than 15°C, especially ranging from -80°C to 15°C and better still less than 10°C, for example ranging from -50°C to 0°C, as described later.

The monomers whose homopolymers have a glass transition temperature of greater than or equal to 40°C are chosen, preferably, from the following monomers, also known as the main monomers:

- methacrylates of formula $CH_2 = C(CH_3)-COOR_1$ in which R_1 represents a linear or branched unsubstituted alkyl group containing from 1 to 4 carbon atoms, such as a methyl, ethyl, propyl or isobutyl group or R_1 represents a C_4 to C_{12} cycloalkyl group,

- acrylates of formula $CH_2 = CH-COOR_2$ in which R_2 represents a C_4 to C_{12} cycloalkyl group such as isobornyl acrylate or a tert-butyl group,

- (meth)acrylamides of formula:



in which R_7 and R_8, which may be identical or different, each represent a hydrogen atom or a linear or branched C_1 to C_{12} alkyl group such as an n-butyl, t-butyl,

isopropyl, isohexyl, isooctyl or isononyl group; or R_7 represents H and R_8 represents a 1,1-dimethyl-3-oxobutyl group,

and R′ denotes H or methyl. Examples of monomers that may be mentioned include N-butylacrylamide, N-t-butylacrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide and N,N-dibutylacrylamide,

- and mixtures thereof.

Main monomers that are particularly preferred are methyl methacrylate, isobutyl (meth)acrylate and isobornyl (meth)acrylate, and mixtures thereof.

b) Block with a Tg of less than or equal to 20°C

The block with a Tg of less than or equal to 20°C has, for example, a Tg ranging from -100 to 20°C, preferably less than or equal to 15°C, especially ranging from -80 to 15°C and better still less than or equal to 10°C, for example ranging from -50 to 0°C.

The block with a Tg of less than or equal to 20°C may be a homopolymer or a copolymer.

In the case where this block is a homopolymer, it is derived from monomers which are such that the homopolymers prepared from these monomers have glass transition temperatures of less than or equal to 20°C. This second block may be a homopolymer consisting of only one type of monomer (for which the Tg of the corresponding homopolymer is less than or equal to 20°C).

In the case where the block with a Tg of less than or equal to 20°C is a copolymer, it may be totally or partially derived from one or more monomers, the nature and concentration of which are chosen such that the Tg of the resulting copolymer is less than or equal to 20°C.

It may comprise, for example

- one or more monomers whose corresponding homopolymer has a Tg of less than or equal to 20°C, for example a Tg ranging from -100 to 20°C, preferably less than 15°C, especially ranging from -80 to 15°C and better still less than 10°C, for example ranging from -50°C to 0°C, and

- one or more monomers whose corresponding homopolymer has a Tg of greater than 20°C, such as monomers with a Tg of greater than or equal to 40°C, for example a Tg ranging from 40 to 150°C, preferably greater than or equal to 50°C, for example ranging from 50°C to 120°C and better still greater than or equal to 60°C, for example ranging from 60°C to 120°C and/or monomers with a Tg of between 20 and 40°C, as described above.

Preferably, the block with a Tg of less than or equal to 20°C is a homopolymer.

The monomers whose homopolymer has a Tg of less than or equal to 20°C are preferably chosen from the following monomers, or main monomers:

- acrylates of formula $CH_2 = CHCOOR_3$, R_3 representing a linear or branched C_1 to C_{12} unsubstituted alkyl group, with the exception of the tert-butyl group, in which one or more hetero atoms chosen from O, N and S is (are) optionally intercalated,

- methacrylates of formula $CH_2 = C(CH_3)-COOR_4$, R_4 representing a linear or branched C_6 to C_{12} unsubstituted alkyl group, in which one or more hetero atoms chosen from O, N and S is (are) optionally intercalated;

- vinyl esters of formula $R_5-CO-O-CH = CH_2$ in which R_5 represents a linear or branched C_4 to C_{12} alkyl group,

- C_4 to C_{12} alkyl vinyl ethers,

- N-(C_4 to C_{12})alkyl acrylamides, such as N-octylacrylamide,

- and mixtures thereof.

The main monomers that are particularly preferred for the block with a Tg of less than or equal to 20°C are alkyl acrylates whose alkyl chain contains from 1 to 10 carbon atoms, with the exception of the tert-butyl group, such as methyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate, and mixtures thereof.

c) Block with a Tg of between 20 and 40°C

The block with a Tg of between 20 and 40°C may be a homopolymer or a copolymer.

In the case where this block is a homopolymer, it is derived from monomers (or main monomers) which are such that the homopolymers prepared from these monomers have glass transition temperatures of between 20 and 40°C. This first block may be a homopolymer, consisting of only one type of monomer (for which the Tg of the corresponding homopolymer ranges from 20°C to 40°C).

The monomers whose homopolymer has a glass transition temperature of between 20 and 40°C are preferably chosen from n-butyl methacrylate, cyclodecyl acrylate, neopentyl acrylate and isodecylacrylamide, and mixtures thereof.

In the case where the block with a Tg of between 20 and 40°C is a copolymer, it is totally or partially derived from one or more monomers (or main monomers) whose nature and concentration are chosen such that the Tg of the resulting copolymer is between 20 and 40°C.

Advantageously, the block with a Tg of between 20 and 40°C is a copolymer totally or partially derived from:

- main monomers whose corresponding homopolymer has a Tg of greater than or equal to 40°C, for example a Tg ranging from 40°C to 150°C, preferably

greater than or equal to 50°C, for example ranging from 50 to 120°C and better still greater than or equal to 60°C, for example ranging from 60°C to 120°C, as described above, and/or

- main monomers whose corresponding homopolymer has a Tg of less than or equal to 20°C, for example a Tg ranging from -100 to 20°C, preferably less than or equal to 15°C, especially ranging from -80°C to 15°C and better still less than or equal to 10°C, for example ranging from -50°C to 0°C, as described above,

the said monomers being chosen such that the Tg of the copolymer forming the first block is between 20 and 40°C.

Such main monomers are chosen, for example, from methyl methacrylate, isobornyl acrylate and methacrylate, butyl acrylate and 2-ethylhexyl acrylate, and mixtures thereof.

Preferably, the proportion of the second block with a Tg of less than or equal to 20°C ranges from 10% to 85% by weight, better still from 20% to 70% and even better still from 20% to 50% by weight of the polymer.

However, each of the blocks may contain in small proportion at least one constituent monomer of the other block.

Thus, the first block may contain at least one constituent monomer of the second block, and vice versa.

Each of the first and/or second blocks may comprise, in addition to the monomers indicated above, one or more other monomers known as additional monomers, which are different from the main monomers mentioned above.

The nature and amount of this or these additional monomer(s) are chosen such that the block in which they are present has the desired glass transition temperature.

This additional monomer is chosen, for example, from:

hydrophilic monomers such as:

- ethylenically unsaturated monomers comprising at least one carboxylic or sulphonic acid function, for instance:
acrylic acid, methacrylic acid, crotonic acid, maleic anhydride, itaconic acid, fumaric acid, maleic acid, acrylamidopropanesulphonic acid, vinylbenzoic acid, vinylphosphoric acid, and salts thereof,

- ethylenically unsaturated monomers comprising at least one tertiary amine function, for instance 2-vinylpyridine, 4-vinylpyridine, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate

and dimethylaminopropylmethacrylamide, and salts thereof,

- methacrylates of formula $CH_2 = C(CH_3)-COOR_6$ in which R_6 represents a linear or branched alkyl group containing from 1 to 4 carbon atoms, such as a methyl, ethyl, propyl or isobutyl group, the said alkyl group being substituted with one or more substituents chosen from hydroxyl groups (for instance 2-hydroxypropyl methacrylate and 2-hydroxyethyl methacrylate) and halogen atoms (Cl, Br, I or F), such as trifluoroethyl methacrylate,

- methacrylates of formula $CH_2 = C(CH_3)-COOR_9$, R_9 representing a linear or branched C_6 to C_{12} alkyl group in which one or more hetero atoms chosen from O, N and S is (are) optionally intercalated, the said alkyl group being substituted with one or more substituents chosen from hydroxyl groups and halogen atoms (Cl, Br, I or F);

- acrylates of formula $CH_2 = CHCOOR_{10}$, R_{10} representing a linear or branched C_1 to C_{12} alkyl group substituted with one or more substituents chosen from hydroxyl groups and halogen atoms (Cl, Br, I or F), such as 2-hydroxypropyl acrylate and 2-hydroxyethyl acrylate, or R_{10} represents a C_1 to C_{12} alkyl-O-POE (polyoxyethylene) with repetition of the oxyethylene unit 5 to 30 times, for example methoxy-POE, or R_8 represents a polyoxyethylene group containing from 5 to

30 ethylene oxide units

b) ethylenically unsaturated monomers comprising one or more silicon atoms, such as methacryloxypropyltrimethoxysilane and methacryloxypropyltris(trimethylsiloxy)silane,

- and mixtures thereof.

Additional monomers that are particularly preferred are acrylic acid, methacrylic acid and trifluoroethyl methacrylate, and mixtures thereof.

According to one preferred embodiment, the block polymer is a non-silicone polymer, i.e. a polymer free of silicon atoms.

This or these additional monomer(s) generally represent(s) an amount of less than or equal to 30% by weight, for example from 1% to 30% by weight, preferably from 5% to 20% by weight and more preferably from 7% to 15% by weight, relative to the total weight of the first and/or second blocks.

Preferably, each of the first and second blocks comprises at least one monomer chosen from (meth)acrylic acid esters, and optionally at least one monomer chosen from (meth)acrylic acid, and mixtures thereof.

Advantageously, each of the first and second blocks is derived entirely from at least one monomer chosen from acrylic acid, (meth)acrylic acid esters and

optionally from at least one monomer chosen from (meth)acrylic acid, and mixtures thereof.

The block polymer may be obtained by free-radical solution polymerization according to the following preparation process:

- a portion of the polymerization solvent is introduced into a suitable reactor and heated until the adequate temperature for the polymerization is reached (typically between 60 and 120°C),
- once this temperature is reached, the constituent monomers of the first block are introduced in the presence of some of the polymerization initiator,
- after a time T corresponding to a maximum degree of conversion of 90%, the constituent monomers of the second block and the rest of the initiator are introduced,
- the mixture is left to react for a time T′ (ranging from 3 to 6 hours), after which the mixture is cooled to room temperature,
- the polymer dissolved in the polymerization solvent is obtained.

The term polymerization solvent means a solvent or a mixture of solvents. The polymerization solvent may be chosen in particular from ethyl acetate, butyl acetate, alcohols such as isopropanol, ethanol, aliphatic alkanes such as isododecane and mixtures

thereof. Preferably, the polymerization solvent is a mixture of butyl acetate and isopropanol or isododecane.

First embodiment

According to a first embodiment, the block polymer comprises a first block with a Tg of greater than or equal to 40°C, as described above in a) and a second block with a Tg of less than or equal to 20°C, as described above in b).

Preferably, the first block with a Tg of greater than or equal to 40°C is a copolymer derived from monomers which are such that the homopolymer prepared from these monomers has a glass transition temperature of greater than or equal to 40°C, such as the monomers described above.

Advantageously, the second block with a Tg of less than or equal to 20°C is a homopolymer derived from monomers which are such that the homopolymer prepared from these monomers has a glass transition temperature of less than or equal to 20°C, such as the monomers described above.

Preferably, the proportion of the block with a Tg of greater than or equal to 40°C ranges from 20% to 90%, better still from 30% to 80% and even better still from 50% to 70% by weight of the polymer. Preferably, the proportion of the block with a Tg of less than or equal to 20°C ranges from 5% to 75%,

preferably from 15% to 50% and better still from 25% to 45% by weight of the polymer.

Advantageously, the block polymer may comprise:

- a first block with a Tg of greater than or equal to 40°C, for example ranging from 85 to 115°C, which is an isobornyl acrylate/isobutyl methacrylate copolymer,

- a second block with a Tg of less than or equal to 20°C, for example ranging from -85 to -55°C, which is a 2-ethylhexyl acrylate homopolymer, and

- an intermediate block, which is an isobornyl acrylate/isobutyl methacrylate/2-ethylhexyl acrylate random copolymer.

Second embodiment

According to a second embodiment, the block polymer comprises a first block having a glass transition temperature (Tg) of between 20 and 40°C, in accordance with the blocks described in c) and a second block having a glass transition temperature of less than or equal to 20°C, as described above in b) or a glass transition temperature of greater than or equal to 40°C, as described in a) above.

Preferably, the proportion of the first block with a Tg of between 20 and 40°C ranges from 10% to 85%, better still from 30% to 80% and even better still from 50% to 70% by weight of the polymer.

When the second block is a block with a Tg of greater than or equal to 40°C, it is preferably present in a proportion ranging from 10% to 85% by weight, better still from 20% to 70% and even better still from 30% to 70% by weight of the polymer.

When the second block is a block with a Tg of less than or equal to 20°C, it is preferably present in a proportion ranging from 10% to 85% by weight, better still from 20% to 70% and even better still from 20% to 50% by weight of the polymer.

Preferably, the first block with a Tg of between 20 and 40°C is a copolymer derived from monomers which are such that the corresponding homopolymer has a Tg of greater than or equal to 40°C, and from monomers which are such that the corresponding homopolymer has a Tg of less than or equal to 20°C.

Advantageously, the second block with a Tg of less than or equal to 20°C or with a Tg of greater than or equal to 40°C is a homopolymer.

According to a first variant, the block polymer comprises:

- a first block with a Tg of between 20 and 40°C, for example with a Tg of 21 to 39°C, which is a copolymer comprising isobornyl acrylate/isobutyl methacrylate/2-ethylhexyl acrylate,

- a second block with a Tg of less than or equal to 20°C, for example ranging from -65 to -35°C,

which is a methyl methacrylate homopolymer, and

- an intermediate block which is an isobornyl acrylate/isobutyl methacrylate/2-ethylhexyl acrylate random copolymer.

According to a second variant, the polymer according to the invention may comprise:

- a first block with a Tg of greater than or equal to 40°C, for example ranging from 85 to 115°C, which is an isobornyl methacrylate/isobutyl methacrylate copolymer,

- a second block with a Tg of less than or equal to 20°C, for example ranging from -35 to -5°C, which is an isobutyl acrylate homopolymer, and

- an intermediate block which is an isobornyl methacrylate/isobutyl methacrylate/isobutyl acrylate random copolymer.

According to a third variant, the polymer according to the invention may comprise:

- a first block with a Tg of greater than or equal to 40°C, for example ranging from 60 to 90°C, which is an isobornyl acrylate/isobutyl methacrylate copolymer,

- a second block with a Tg of less than or equal to 20°C, for example ranging from -35 to -5°C, which is an isobutyl acrylate homopolymer, and

- an intermediate block which is an isobornyl acrylate/isobutyl methacrylate/isobutyl acrylate random

copolymer.

The block polymer may be present in the composition according to the invention in a dry matter (or active material) content ranging from 5 to 55%, preferably ranging from 6 to 45% and better still from 8 to 40% by weight relative to the total weight of the composition.

2) Cosmetically acceptable organic liquid medium

The term "organic liquid medium" means a medium containing at least one organic compound that is liquid at room temperature (25°C) and atmospheric pressure (10^5 Pa) such as the organic oils and solvents commonly used in cosmetic compositions.

According to a particularly preferred embodiment, the organic liquid medium of the composition contains at least one organic liquid which is the or one of the organic solvent(s) for polymerizing the block polymer as described above. Advantageously, the said organic polymerization solvent is the major organic liquid by weight in the organic liquid medium of the cosmetic composition.

The organic liquid medium of the composition may represent from 10 to 95%, preferably from 20 to 90%, and better still from 30 to 80% by weight relative to the total weight of the composition.

The organic oils or solvents can form especially a fatty phase, and in particular a

continuous fatty phase. The composition may be an anhydrous composition.

The cosmetically acceptable organic liquid medium of the composition advantageously comprises at least one volatile organic solvent or oil defined below.

For the purposes of the invention, the expression "volatile organic solvent or oil" means any non-aqueous medium that can evaporate on contact with the keratin fibre in less than one hour at room temperature and atmospheric pressure. The volatile organic solvent(s) and the volatile oils of the invention are organic solvents and volatile cosmetic oils, that are liquid at room temperature, having a non-zero vapour pressure at room temperature and atmospheric pressure, ranging from 0.13 Pa to 40 000 Pa (10^{-3} to 300 mmHg), in particular ranging from 1.3 Pa to 13 000 Pa (0.01 to 100 mmHg) and more particularly ranging from 1.3 Pa to 1300 Pa (0.01 to 10 mmHg). The expression "non-volatile oil" means an oil that remains on the keratin fibre at room temperature and atmospheric pressure for at least several hours and which in particular has a vapour pressure of less than 10^{-3} mmHg (0.13 Pa).

These oils may be hydrocarbon-based oils, silicone oils, or mixtures thereof.

The expression "hydrocarbon-based oil" means

an oil mainly containing hydrogen and carbon atoms and optionally oxygen, nitrogen, sulphur or phosphorus atoms. The volatile hydrocarbon-based oils may be chosen from hydrocarbon-based oils containing from 8 to 16 carbon atoms, and especially C_8-C_{16} branched alkanes, for instance C_8-C_{16} isoalkanes of petroleum origin (also known as isoparaffins), for instance isododecane (also known as 2,2,4,4,6-pentamethylheptane), isodecane and isohexadecane, and, for example, the oils sold under the trade names Isopars or Permetyls, C_8-C_{16} branched esters, isohexyl neopentanoate, and mixtures thereof. Other volatile hydrocarbon-based oils, for instance petroleum distillates, especially those sold under the name Shell Solt by the company Shell, may also be used. The volatile solvent is preferably chosen from hydrocarbon-based volatile oils containing from 8 to 16 carbon atoms, and mixtures thereof.

Volatile oils which may also be used are volatile silicones such as, for example, linear or cyclic volatile silicone oils, especially those with a viscosity $\leq$ 6 centistokes (6×10^{-6} m^2/s) and especially containing from 2 to 10 silicon atoms, these silicones optionally comprising alkyl or alkoxy groups containing from 1 to 22 carbon atoms. As volatile silicone oils which may be used in the invention, mention may be made in particular of octamethylcyclotetrasiloxane, deca-methylcyclopentasiloxane, dodecamethylcyclohexa-

siloxane, heptamethylhexyltrisiloxane, heptamethyloctyltrisiloxane, hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane and dodecamethylpentasiloxane, and mixtures thereof.

The volatile oil may be present in the composition according to the invention in a content ranging from 0.5% to 95% by weight and preferably from 1 to 65% by weight and better still from 5 to 40% by weight relative to the total weight of the composition.

The non-volatile silicone oils which may be used in the composition according to the invention may be non-volatile polydimethylsiloxanes (PDMSs), polydimethylsiloxanes comprising alkyl or alkoxy groups, that are pendent and/or at the end of a silicone chain, the groups each containing from 2 to 24 carbon atoms, phenylsilicones, for instance phenyltrimethicones, phenyldimethicones, phenyltrimethylsiloxydiphenylsiloxanes, diphenyldimethicones, diphenylmethyldiphenyltrisiloxanes and 2-phenylethyl trimethylsiloxysilicates.

The fluoro oils which can be used in the composition of the invention are especially fluorosilicone oils, polyfluoro ethers, fluorosilicones as described in the document EP-A-847752.

The non-volatile oils may be present in the composition according to the invention in a content ranging from 0 to 30% (especially from 0.1 to 30%) by

weight, preferably from 0 to 20% by weight (especially 0.1 to 20%) and better still from 0 to 10% by weight (especially 0.1% to 10%), relative to the total weight of the composition.

In one embodiment of the invention, the organic liquid medium of the composition comprises at least one volatile organic oil which is the solvent for polymerizing the block polymer and in which the block polymer is advantageously soluble. Preferably, this volatile organic oil is isododecane. Such a composition has the advantage of being easy to remove when used as makeup, with a conventional makeup-removing product for waterproof mascaras.

The composition according to the invention may comprise an aqueous medium, constituting an aqueous phase, which can form the continuous phase of the composition.

The aqueous phase may consist mainly of water; it may also comprise a mixture of water and a water-miscible solvent (miscibility in water greater than 50% by weight at 25°C) such as lower monoalcohols having from 1 to 5 carbon atoms such as ethanol, isopropanol, glycols having from 2 to 8 carbon atoms such as propylene glycol, ethylene glycol, 1,3-butylene glycol, dipropylene glycol, C_3-C_4 ketones, C_2-C_4 aldehydes and mixtures thereof.

The aqueous phase (water and optionally the

water-miscible solvent) may be present in a content ranging from 1% to 95% by weight, preferably ranging from 3% to 80% by weight, and preferentially ranging from 5% to 60% by weight, relative to the total weight of the composition.

Wax

The composition according to the invention may comprise a wax or a mixture of waxes.

The wax under consideration in the context of the present invention is generally a lipophilic compound that is solid at room temperature (25°C), with a solid/liquid reversible change of state, having a melting point of greater than or equal to 30°C, which may be up to 120°C.

By bringing the wax to the liquid form (melting), it is possible to make it miscible with oils and to form a microscopically uniform mixture, but on bringing the mixture back to room temperature, recrystallization of the wax in the oils of the mixture is obtained.

In particular, the waxes that are suitable for the invention may have a melting point of greater than about 45°C and in particular greater than 55°C.

The melting point of the wax may be measured using a differential scanning calorimeter (DSC), for example the calorimeter sold under the name DSC 30 by the company Metler.

The measuring protocol is as follows:

A sample of 15 mg of product placed in a crucible is subjected to a first temperature rise ranging from 0°C to 120°C, at a heating rate of 10°C/minute, it is then cooled from 120°C to 0°C at a cooling rate of 10°C/minute and is finally subjected to a second temperature increase ranging from 0°C to 120°C at a heating rate of 5°C/minute. During the second temperature increase, the variation of the difference in power absorbed by the empty crucible and by the crucible containing the sample of product is measured as a function of the temperature. The melting point of the compound is the temperature value corresponding to the top of the peak of the curve representing the variation in the difference in absorbed power as a function of the temperature.

The waxes that may be used in the compositions according to the invention are chosen from waxes that are solid and rigid at room temperature, of animal, plant, mineral or synthetic origin and mixtures thereof.

The wax may also have a hardness ranging from 0.05 MPa to 30 MPa, preferably ranging from 6 MPa to 15 MPa. The hardness is determined by measuring the compression force, measured at 20°C using a texturometer sold under the name TA-TX2i by the company Rheo, equipped with a stainless-steel cylindrical

spindle 2 mm in diameter, travelling at a measuring speed of 0.1 mm/s, and penetrating into the wax to a penetration depth of 0.3 mm.

The measuring protocol is as follows:

The wax is melted at a temperature equal to the melting point of the wax + 20°C. The molten wax is poured into a container 30 mm in diameter and 20 mm deep. The wax is recrystallized at room temperature (25°C) for 24 hours and is then stored for at least 1 hour at 20°C, before performing the hardness measurement. The hardness value is the maximum compression force measured, divided by the area of the texturometer spindle in contact with the wax.

Hydrocarbon-based waxes, for instance beeswax, lanolin wax, Chinese insect waxes, rice wax, carnauba wax, candelilla wax, ouricurry wax, esparto grass wax, cork fibre wax, sugar cane wax, Japan wax and sumac wax; montan wax, microcrystalline waxes, paraffins and ozokerite; polyethylene waxes, the waxes obtained by Fischer-Tropsch synthesis and waxy copolymers, and also esters thereof, may especially be used.

Mention may also be made of waxes obtained by catalytic hydrogenation of animal or plant oils containing linear or branched C_8-C_{32} fatty chains.

Among these, mention may be made especially of hydrogenated jojoba oil, isomerized jojoba oil such

as the partially hydrogenated trans-isomerized jojoba oil manufactured or sold by the company Desert Whale under the commercial reference Iso-Jojoba-50®, hydrogenated sunflower oil, hydrogenated castor oil, hydrogenated coconut oil and hydrogenated lanolin oil, bis(1,1,1-trimethylolpropane) tetrastearate sold under the name "Hest 2T-4S" by the company Heterene and bis(1,1,1-trimethylolpropane) tetrabehenate sold under the name Hest 2T-4B by the company Heterene.

Mention may also be made of silicone waxes and fluoro waxes.

It is also possible to use the wax obtained by hydrogenation of olive oil esterified with stearyl alcohol, sold under the name "Phytowax Olive 18 L 57" or the waxes obtained by hydrogenation of castor oil esterified with cetyl alcohol, sold under the name "Phytowax Ricin 16L64 and 22L73" by the company Sophim. Such waxes are described in patent application FR-A-2 792 190.

According to an advantageous embodiment, the composition according to the invention comprises at least one wax called "hard wax" which has a hardness greater than or equal to 6 MPa, in particular ranging from 6 MPa to 30 MPa, and preferably greater than or equal to 7 MPa, in particular ranging from 7 MPa to 25 MPa, and even better greater than or equal to 8 MPa,

in particular from 8 to 25 MPa, better still greater than or equal to 9 MPa, for example from 9 to 20 MPa.

The hardness of the hard wax is measured according to the same protocol described above.

As hard wax, use may be made of Carnauba wax, Candelilla wax, polyethylene waxes, hydrogenated jojoba oil, sumac wax, ceresine, octacosanyl stearate, tetracontanyl stearate, Shellac wax, behenyl fumarate and di-(1,1,1-trimethylolpropane) tetrastearate sold under the name "Hest 2T-4S" by the company Heterene, di-(1,1,1-trimethylolpropane) tetrabehenate sold under the name Hest 2T-4B by the company Heterene, ozokerites such as that sold under the name Ozokerite Wax SP 1020 P" by the company Strahl & Pitsch, the wax obtained by hydrogenation of olive oil esterified with stearyl alcohol sold under the name Phytowax Olive 18 L 57 by the company Sophim.

The hard wax may be present in the composition according to the invention in a content ranging from 0.1% to 30% by weight, relative to the total weight of the composition, preferably ranging from 1% to 20% by weight, and more preferably ranging from 2% to 10% by weight.

The composition according to the invention may comprise a total wax content ranging from 1 to 50% by weight, in particular it may comprise from 5 to 30% by weight, and more particularly from 10 to 30% by

weight relative to the total weight of the composition.

The wax(es) may be in the form of an aqueous microdispersion of wax. The expression "aqueous microdispersion of wax" means an aqueous dispersion of wax particles in which the size of the said wax particles is less than or equal to about 1 µm.

Wax microdispersions are stable dispersions of colloidal wax particles, and are described especially in "Microemulsions Theory and Practice", L.M. Prince Ed., Academic Press (1977) pages 21-32.

In particular, these wax microdispersions may be obtained by melting the wax in the presence of a surfactant, and optionally of a portion of water, followed by gradual addition of hot water with stirring. The intermediate formation of an emulsion of the water-in-oil type is observed, followed by a phase inversion, with final production of a microemulsion of the oil-in-water type. On cooling, a stable microdispersion of solid wax colloidal particles is obtained.

The wax microdispersions may also be obtained by stirring the mixture of wax, surfactant and water using stirring means such as ultrasound, high-pressure homogenizers or turbomixers.

The particles of the wax microdispersion preferably have mean sizes of less than 1 µm (especially ranging from 0.02 µm to 0.99 µm) and

preferably less than 0.5 µm (especially ranging from 0.06 µm to 0.5 µm).

These particles consist essentially of a wax or a mixture of waxes. However, they may comprise a small proportion of oily and/or pasty fatty additives, a surfactant and/or a common liposoluble additive/active agent.

In some cases and depending on the wishes of consumers, it is desirable to prepare cosmetic compositions having the advantages described above and exhibiting a glossy appearance. Accordingly, another subject of the present invention is a wax-free composition for coating keratin fibres comprising a cosmetically acceptable liquid organic medium and a film-forming linear ethylenic block polymer, the said polymer being such that when it is present in a sufficient quantity in the composition, it is capable of forming a film exhibiting a staying power greater than or equal to 12 hours.

The term "wax-free" means a composition comprising less than 2% of waxes, preferably less than 1% and better still less than 0.5% of waxes.

Such a wax-free composition also has the advantage of making it possible particularly smooth, homogeneous and nongranular of the deposit.

Another subject of the present invention is the use of a wax-free composition for coating keratin

fibres, comprising, in a cosmetically acceptable liquid organic medium, a film-forming linear ethylenic block polymer to obtain a film that is deposited on the said keratin materials, that is smooth and homogeneous and has a glossy appearance.

Such a wax-free composition may be used in particular as top coat, that is to say as a composition to be applied over a mascara base coat in order to improve the staying power of the said mascara.

The composition according to the invention may contain at least one fatty compound that is pasty at room temperature. For the purposes of the invention, the expression "pasty fatty substance" means fatty substances with a melting point ranging from 20 to 55°C, preferably 25 to 45°C, and/or a viscosity at 40°C ranging from 0.1 to 40 Pa.s (1 to 400 poises), preferably 0.5 to 25 Pa.s, measured using a Contraves TV or Rheomat 80 viscometer, equipped with a spindle rotating at 60 Hz. A person skilled in the art can select the spindle for measuring the viscosity from the spindles MS-r3 and MS-r4, on the basis of his general knowledge, so as to be able to carry out the measurement of the pasty compound tested.

These fatty substances are preferably hydrocarbon-based compounds, optionally of polymeric type; they can also be chosen from silicone compounds; they may also be in the form of a mixture of

hydrocarbon-based compounds and/or silicone compounds. In the case of a mixture of different pasty fatty substances, the hydrocarbon-based pasty compounds (containing mainly hydrogen and carbon atoms and optionally ester groups) are preferably used in major proportion.

Among the pasty compounds which may be used in the composition according to the invention, mention may be made of lanolins and lanolin derivatives such as acetylated lanolins or oxypropylenated lanolins or isopropyl lanolate, having a viscosity of from 18 to 21 Pa.s, preferably 19 to 20.5 Pa.s, and/or a melting point of from 30 to 55°C, and mixtures thereof. It is also possible to use esters of fatty acids or of fatty alcohols, in particular those containing from 20 to 65 carbon atoms (melting point of about from 20 to 35°C and/or viscosity at 40°C ranging from 0.1 to 40 Pa.s), such as triisostearyl or cetyl citrate; arachidyl propionate; polyvinyl laurate; cholesterol esters, such as triglycerides of plant origin, such as hydrogenated plant oils, viscous polyesters such as poly(12-hydroxystearic acid), and mixtures thereof.

Mention may also be made of pasty silicone fatty substances such as polydimethylsiloxanes (PDMSs) containing pendent chains of the alkyl or alkoxy type containing from 8 to 24 carbon atoms, and having a melting point of 20-55°C, such as stearyldimethicones,

in particular those sold by Dow Corning under the trade names DC2503 and DC25514, and mixtures thereof.

The pasty fatty substance may be present in the composition according to the invention in a proportion of from 0.01% to 60% by weight, relative to the total weight of the composition, preferably ranging from 0.5% to 45% by weight, and better still ranging from 2% to 30% by weight, in the composition.

The composition according to the invention can contain emulsifying surfactants, present in particular in a proportion ranging from 2% to 30% by weight relative to the total weight of the composition, and better still from 5% to 15%. These surfactants may be chosen from anionic and nonionic surfactants. Reference may be made to the document "Encyclopedia of Chemical Technology, Kirk-Othmer", volume 22, pp. 333-432, 3rd edition, 1979, Wiley, for the definition of the properties and functions (emulsifying) of surfactants, in particular pp. 347-377 of the said reference, for the anionic and nonionic surfactants.

The surfactants preferably used in the composition according to the invention are chosen from:

- nonionic surfactants: fatty acids, fatty alcohols, polyethoxylated or polyglycerolated fatty alcohols such as polyethoxylated stearyl or cetylstearyl alcohol, fatty acid esters of sucrose,

alkylglucose esters, in particular polyoxyethylenated fatty esters of C_1-C_6 alkyl glucose, and mixtures thereof;

- anionic surfactants: C_{16}-C_{30} fatty acids neutralized with amines, aqueous ammonia or alkaline salts, and mixtures thereof.

Surfactants that make it possible to obtain an oil-in-water or wax-in-water emulsion are preferably used.

The composition according to the invention may comprise, in addition to the block polymer described above according to the invention, an additional polymer such as a film-forming polymer.

The film-forming polymer may be present in the composition according to the invention in a dry matter content ranging from 0.1% to 60% by weight, preferably from 0.5% to 40% by weight and better still from 1% to 30% by weight relative to the total weight of the composition.

In the present application, the expression "film-forming polymer" means a polymer that is capable, by itself or in the presence of an auxiliary film-forming agent, of forming a continuous and adherent film on a support, in particular on keratin materials such as the eyelashes.

Among the film-forming polymers that may be used in the composition of the present invention,

mention may be made of synthetic polymers, of radical-mediated type or of polycondensate type, polymers of natural origin, and mixtures thereof.

The expression "radical-mediated film-forming polymer" means a polymer obtained by polymerization of monomers containing unsaturation, in particular ethylenic unsaturation, each monomer being capable of homopolymerizing (unlike polycondensates).

The film-forming polymers of radical-mediated type may be, in particular, vinyl polymers or copolymers, in particular acrylic polymers.

The vinyl film-forming polymers can result from the polymerization of monomers containing ethylenic unsaturation and containing at least one acidic group and/or esters of these acidic monomers and/or amides of these acidic monomers.

Monomers bearing an acidic group which may be used are α,β-ethylenic unsaturated carboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, maleic acid or itaconic acid. (Meth)acrylic acid and crotonic acid are preferably used, and more preferably (meth)acrylic acid.

The esters of acidic monomers are advantageously chosen from (meth)acrylic acid esters (also known as (meth)acrylates), especially (meth)acrylates of an alkyl, in particular of a C_1-C_{30} and preferably C_1-C_{20} alkyl, (meth)acrylates of an aryl,

in particular of a C_6-C_{10} aryl, and (meth)acrylates of a hydroxyalkyl, in particular of a C_2-C_6 hydroxyalkyl.

Among the alkyl (meth)acrylates that may be mentioned are methyl methacrylate, ethyl methacrylate, butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, lauryl methacrylate and cyclohexyl methacrylate.

Among the hydroxyalkyl (meth)acrylates that may be mentioned are hydroxyethyl acrylate, 2-hydroxypropyl acrylate, hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate.

Among the aryl (meth)acrylates that may be mentioned are benzyl acrylate and phenyl acrylate.

The (meth)acrylic acid esters that are particularly preferred are the alkyl (meth)acrylates.

According to the present invention, the alkyl group of the esters may be either fluorinated or perfluorinated, i.e. some or all of the hydrogen atoms of the alkyl group are substituted with fluorine atoms.

Examples of amides of the acid monomers that may be mentioned are (meth)acrylamides, and especially N-alkyl(meth)acrylamides, in particular of a C_2-C_{12} alkyl. Among the N-alkyl(meth)acrylamides that may be mentioned are N-ethylacrylamide, N-t-butylacrylamide, N-t-octylacrylamide and N-undecylacrylamide.

The vinyl film-forming polymers may also result from the homopolymerization or copolymerization

of monomers chosen from vinyl esters and styrene monomers. In particular, these monomers may be polymerized with acid monomers and/or esters thereof and/or amides thereof, such as those mentioned above.

Examples of vinyl esters that may be mentioned are vinyl acetate, vinyl neodecanoate, vinyl pivalate, vinyl benzoate and vinyl t-butylbenzoate.

Styrene monomers that may be mentioned are styrene and α-methylstyrene.

Among the film-forming polycondensates that may be mentioned are polyurethanes, polyesters, polyesteramides, polyamides, epoxyester resins and polyureas.

The polyurethanes may be chosen from anionic, cationic, nonionic and amphoteric polyurethanes, polyurethane-acrylics, polyurethane-polyvinyl-pyrrolidones, polyester-polyurethanes, polyether-polyurethanes, polyureas and polyurea/polyurethanes, and mixtures thereof.

The polyesters may be obtained, in a known manner, by polycondensation of dicarboxylic acids with polyols, in particular diols.

The dicarboxylic acid may be aliphatic, alicyclic or aromatic. Examples of such acids that may be mentioned are: oxalic acid, malonic acid, dimethylmalonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, 2,2-dimethylglutaric acid,

azelaic acid, suberic acid, sebacic acid, fumaric acid, maleic acid, itaconic acid, phthalic acid, dodecanedioic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, isophthalic acid, terephthalic acid, 2,5-norbornanedicarboxylic acid, diglycolic acid, thiodipropionic acid, 2,5-naphthalenedicarboxylic acid or 2,6-naphthalenedicarboxylic acid. These dicarboxylic acid monomers may be used alone or as a combination of at least two dicarboxylic acid monomers. Among these monomers, the ones preferentially chosen are phthalic acid, isophthalic acid and terephthalic acid.

The diol may be chosen from aliphatic, alicyclic and aromatic diols. The diol used is preferably chosen from: ethylene glycol, diethylene glycol, triethylene glycol, 1,3-propanediol, cyclohexanedimethanol and 4-butanediol. Other polyols that may be used are glycerol, pentaerythritol, sorbitol and trimethylolpropane.

The polyesteramides may be obtained in a manner analogous to that of the polyesters, by polycondensation of diacids with diamines or amino alcohols. Diamines that may be used are ethylenediamine, hexamethylenediamine and meta- or para-phenylenediamine. An amino alcohol that may be used is monoethanolamine.

The polyester may also comprise at least one

monomer bearing at least one group $-SO_3M$, with M representing a hydrogen atom, an ammonium ion NH_4^+ or a metal ion such as, for example, an Na^+, Li^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Fe^{2+} or Fe^{3+} ion. A difunctional aromatic monomer comprising such a group $-SO_3M$ may be used in particular.

The aromatic nucleus of the difunctional aromatic monomer also bearing a group $-SO_3M$ as described above may be chosen, for example, from benzene, naphthalene, anthracene, biphenyl, oxybiphenyl, sulphonylbiphenyl and methylenebiphenyl nuclei. As examples of difunctional aromatic monomers also bearing a group $-SO_3M$, mention may be made of: sulphoisophthalic acid, sulphoterephthalic acid, sulphophthalic acid, 4-sulphonaphthalene-2,7-dicarboxylic acid.

The copolymers preferably used are those based on isophthalate/sulphoisophthalate, and more particularly copolymers obtained by condensation of diethylene glycol, cyclohexanedimethanol, isophthalic acid and sulphoisophthalic acid.

The polymers of natural origin, optionally modified, may be chosen from shellac resin, sandarac gum, dammar resins, elemi gums, copal resins and cellulose polymers, and mixtures thereof.

According to a first embodiment of the composition according to the invention, the film-forming polymer may be a water-soluble polymer and may

be present in an aqueous phase of the composition; the polymer is thus solubilized in the aqueous phase of the composition. Examples of water-soluble film-forming polymers that may be mentioned are:

- proteins, for instance proteins of plant origin such as wheat proteins and soybean proteins; proteins of animal origin such as keratins, for example keratin hydrolysates and sulphonic keratins;
- polymers of cellulose such as hydroxyethylcellulose, hydroxypropylcellulose, methylcellulose, ethylhydroxyethylcellulose and carboxymethylcellulose, and quaternized cellulose derivatives;
- acrylic polymers or copolymers, such as polyacrylates or polymethacrylates;
- vinyl polymers, for instance polyvinylpyrrolidones, copolymers of methyl vinyl ether and of malic anhydride, the copolymer of vinyl acetate and of crotonic acid, copolymers of vinylpyrrolidone and of vinyl acetate; copolymers of vinylpyrrolidone and of caprolactam; polyvinyl alcohol;
- polymers of natural origin, which are optionally modified, such as:
- gum arabics, guar gum, xanthan derivatives, karaya gum;
- alginates and carrageenans;
- glycosaminoglycans, hyaluronic acid and derivatives thereof;

- shellac resin, sandarac gum, dammar resins, elemi gums and copal resins;
- deoxyribonucleic acid;
- mucopolysaccharides such as chondroitin sulphate,

and mixtures thereof.

According to another embodiment of the composition according to the invention, the film-forming polymer may be a polymer dissolved in a liquid fatty phase comprising organic solvents or oils such as those described above (the film-forming polymer is thus said to be a liposoluble polymer). For the purposes of the invention, the expression "liquid fatty phase" means a fatty phase which is liquid at room temperature (25°C) and atmospheric pressure (760 mmHg, i.e. 10^5 Pa), composed of one or more fatty substances that are liquid at room temperature, such as the oils described above, which are generally mutually compatible.

The liquid fatty phase preferably comprises a volatile oil, optionally mixed with a non-volatile oil, the oils possibly being chosen from those mentioned above.

Examples of liposoluble polymers which may be mentioned are copolymers of vinyl ester (the vinyl group being directly linked to the oxygen atom of the ester group and the vinyl ester containing a saturated, linear or branched hydrocarbon-based radical of 1 to 19 carbon atoms, linked to the carbonyl of the ester

group) and of at least one other monomer which may be a vinyl ester (other than the vinyl ester already present), an α-olefin (containing from 8 to 28 carbon atoms), an alkyl vinyl ether (in which the alkyl group comprises from 2 to 18 carbon atoms) or an allylic or methallylic ester (containing a saturated, linear or branched hydrocarbon-based radical of 1 to 19 carbon atoms, linked to the carbonyl of the ester group).

These copolymers may be crosslinked with the aid of crosslinking agents, which may be either of the vinyl type or of the allylic or methallylic type, such as tetraallyloxyethane, divinylbenzene, divinyl octanedioate, divinyl dodecanedioate and divinyl octadecanedioate.

Examples of these copolymers which may be mentioned are the following copolymers: vinyl acetate/allyl stearate, vinyl acetate/vinyl laurate, vinyl acetate/vinyl stearate, vinyl acetate/octadecene, vinyl acetate/octadecyl vinyl ether, vinyl propionate/allyl laurate, vinyl propionate/vinyl laurate, vinyl stearate/1-octadecene, vinyl acetate/1-dodecene, vinyl stearate/ethyl vinyl ether, vinyl propionate/cetyl vinyl ether, vinyl stearate/allyl acetate, vinyl 2,2-dimethyloctanoate/vinyl laurate, allyl 2,2-dimethylpentanoate/vinyl laurate, vinyl dimethylpropionate/vinyl stearate, allyl dimethylpropionate/vinyl stearate, vinyl propionate/vinyl stearate,

crosslinked with 0.2% divinylbenzene, vinyl dimethylpropionate/vinyl laurate, crosslinked with 0.2% divinylbenzene, vinyl acetate/octadecyl vinyl ether, crosslinked with 0.2% tetraallyloxyethane, vinyl acetate/allyl stearate, crosslinked with 0.2% divinylbenzene, vinyl acetate/1-octadecene, crosslinked with 0.2% divinylbenzene, and allyl propionate/allyl stearate, crosslinked with 0.2% divinylbenzene.

Examples of liposoluble film-forming polymers which may also be mentioned are liposoluble copolymers, and in particular those resulting from the copolymerization of vinyl esters containing from 9 to 22 carbon atoms or of alkyl acrylates or methacrylates, and alkyl radicals containing from 10 to 20 carbon atoms.

Such liposoluble copolymers may be chosen from copolymers of polyvinyl stearate, polyvinyl stearate crosslinked with the aid of divinylbenzene, of diallyl ether or of diallyl phthalate, polystearyl (meth)acrylate, polyvinyl laurate and polylauryl (meth)acrylate, it being possible for these poly(meth)acrylates to be crosslinked with the aid of ethylene glycol dimethacrylate or tetraethylene glycol dimethacrylate.

The liposoluble copolymers defined above are known and are described in particular in patent application FR-A-2 232 303; they may have a weight-

average molecular weight ranging from 2 000 to 500 000 and preferably from 4 000 to 200 000.

As liposoluble film-forming polymers which may be used in the invention, mention may also be made of polyalkylenes and in particular copolymers of C_2-C_{20} alkenes, such as polybutene, alkylcelluloses with a linear or branched, saturated or unsaturated C_1-C_8 alkyl radical, for instance ethylcellulose and propylcellulose, copolymers of vinylpyrrolidone (VP) and in particular copolymers of vinylpyrrolidone and of C_2 to C_{40} and better still C_3 to C_{20} alkene. As examples of VP copolymers which may be used in the invention, mention may be made of the copolymers of VP/vinyl acetate, VP/ethyl methacrylate, butylated polyvinylpyrrolidone (PVP), VP/ethyl methacrylate/methacrylic acid, VP/eicosene, VP/hexadecene, VP/triacontene, VP/styrene or VP/acrylic acid/lauryl methacrylate.

The film-forming polymer may also be present in the composition in the form of particles dispersed in an aqueous phase or in a non-aqueous solvent phase, which is generally known as a latex or pseudolatex. The techniques for preparing these dispersions are well known to those skilled in the art.

Aqueous dispersions of film-forming polymers which may be used are the acrylic dispersions sold under the names Neocryl XK-90®, Neocryl A-1070®, Neocryl A-1090®, Neocryl BT-62®, Neocryl A-1079® and

Neocryl A-523® by the company Avecia-Neoresins, Dow Latex 432® by the company Dow Chemical, Daitosol 5000 AD® or Daitosol 5000 SJ by the company Daito Kasey Kogyo; Syntran 5760 by the company Interpolymer or the aqueous dispersions of polyurethane sold under the names Neorez R-981® and Neorez R-974® by the company Avecia-Neoresins, Avalure UR-405®, Avalure UR-410®, Avalure UR-425®, Avalure UR-450®, Sancure 875®, Sancure 861®, Sancure 878® and Sancure 2060® by the company Goodrich, Impranil 85® by the company Bayer and Aquamere H-1511® by the company Hydromer; the sulphopolyesters sold under the brand name "Eastman AQ®" by the company Eastman Chemical Products, vinyl dispersions, for instance "Mexomer PAM" and also acrylic dispersions in isododecane, for instance "Mexomer PAP" by the company Chimex.

According to one embodiment, the composition according to the invention advantageously comprises a film-forming linear ethylenic block polymer as described above and particles of film-forming polymer dispersed in an aqueous phase.

The composition according to the invention may comprise a plasticizer, which promotes the formation of a film with the film-forming polymer. Such a plasticizer may be chosen from any of the compounds known to those skilled in the art as being capable of satisfying the desired function.

<u>Additives</u>

The composition according to the invention may also comprise a dyestuff, for instance pulverulent dyestuffs, liposoluble dyes and water-soluble dyes. This dyestuff may be present in a content ranging from 0.01% to 30% by weight relative to the total weight of the composition.

The pulverulent dyestuffs may be chosen from pigments and nacres.

The pigments may be white or coloured, mineral and/or organic, and coated or uncoated. Among the mineral pigments which may be mentioned are titanium dioxide, optionally surface-treated, zirconium oxide, zinc oxide or cerium oxide, as well as iron oxide, chromium oxide, manganese violet, ultramarine blue, chromium hydrate and ferric blue. Among the organic pigments that may be mentioned are carbon black, pigments of D & C type, and lakes based on cochineal carmine or on barium, strontium, calcium or aluminium.

The nacres may be chosen from white nacreous pigments such as mica coated with titanium or with bismuth oxychloride, coloured nacreous pigments such as titanium mica with iron oxides, titanium mica with, in particular, ferric blue or chromium oxide, titanium mica with an organic pigment of the abovementioned

type, and nacreous pigments based on bismuth oxychloride.

The liposoluble dyes are, for example, Sudan Red, D&C Red 17, D&C Green 6, β-carotene, soybean oil, Sudan Brown, D&C Yellow 11, D&C Violet 2, D&C Orange 5, quinoline yellow and annatto. The water-soluble dyes are, for example, beetroot juice, methylene blue, the disodium salt of ponceau, the disodium salt of alizarin green, quinoline yellow, the trisodium salt of amaranthus, the disodium salt of tartrazine, the monosodium salt of rhodamine, the disodium salt of fuchsin, and xanthophyll.

The fillers may be chosen from those that are well known to a person skilled in the art and commonly used in cosmetic compositions. The fillers may be mineral or organic and lamellar or spherical. Mention may be made of talc, mica, silica, kaolin, polyamide powder for instance Nylon® (Orgasol from Atochem), poly-β-alanine powder and polyethylene powder, tetrafluoroethylene polymer powders for instance Teflon®, lauroyllysine, starch, boron nitride, expanded hollow polymer microspheres such as those made of polyvinylidene chloride/acrylonitrile, for instance Expancel® (Nobel Industrie), acrylic powders such as Polytrap® (Dow Corning), polymethyl methacrylate particles and silicone resin microbeads (for example Tospearls® from Toshiba), precipitated calcium

carbonate, magnesium carbonate, magnesium hydrocarbonate, hydroxyapatite, hollow silica microspheres (Silica Beads® from Maprecos), glass or ceramic microcapsules, and metal soaps derived from organic carboxylic acids containing from 8 to 22 carbon atoms and preferably from 12 to 18 carbon atoms, for example zinc, magnesium or lithium stearate, zinc laurate or magnesium myristate.

The fillers may represent from 0.1% to 25% and better still from 1% to 20% by weight relative to the total weight of the composition.

The composition of the invention may additionally comprise any additive commonly used in cosmetics, such as antioxidants, preservatives, fragrances, neutralizing agents, gelling agents, thickeners, vitamins and mixtures thereof.

The gelling agents that may be used in the compositions according to the invention may be organic or mineral, and polymeric or molecular, hydrophilic or lipophilic gelling agents.

Mineral lipophilic gelling agents that may be mentioned include optionally modified clays, for instance hectorites modified with a C_{10} to C_{22} fatty acid ammonium chloride, for instance hectorite modified with distearyldimethylammonium chloride, for instance the product sold under the name "Bentone 38V®" by the company Elementis.

Mention may also be made of fumed silica optionally subjected to a hydrophobic surface treatment, the particle size of which is less than 1 µm. Specifically, it is possible to chemically modify the surface of the silica, by chemical reaction generating a reduced number of silanol groups present at the surface of the silica. It is especially possible to substitute silanol groups with hydrophobic groups: a hydrophobic silica is then obtained. The hydrophobic groups may be:

- trimethylsiloxyl groups, which are obtained especially by treating fumed silica in the presence of hexamethyldisilazane. Silicas thus treated are known as "silica silylate" according to the CTFA (6th edition, 1995). They are sold, for example, under the references "Aerosil R812®" by the company Degussa, and "Cab-O-Sil TS-530®" by the company Cabot;

- dimethylsilyloxyl or polydimethylsiloxane groups, which are obtained especially by treating fumed silica in the presence of polydimethylsiloxane or dimethyldichlorosilane. Silicas thus treated are known as "silica dimethyl silylate" according to the CTFA (6th edition, 1995). They are sold, for example, under the references "Aerosil R972®" and "Aerosil R974®" by the company Degussa, and "Cab-O-Sil TS-610®" and "Cab-O-Sil TS-720®" by the company Cabot.

The hydrophobic fumed silica particularly has a particle size that may be nanometric to micrometric, for example ranging from about 5 to 200 nm.

The polymeric organic lipophilic gelling agents are, for example, partially or totally crosslinked elastomeric organopolysiloxanes of three-dimensional structure, for instance those sold under the names "KSG6®", "KSG16®" and "KSG18®" from Shin-Etsu, "Trefil E-505C®" and "Trefil E-506C®" from Dow Corning, "Gransil SR-CYC®", "SR DMF 10®", "SR-DC556®", "SR 5CYC gel®", "SR DMF 10 gel®" and "SR DC 556 gel®" from Grant Industries and "SF 1204®" and "JK 113®" from General Electric; ethylcellulose, for instance that sold under the name "Ethocel®" by Dow Chemical and galactomannans comprising from one to six and in particular from two to four hydroxyl groups per monosaccharide, substituted with a saturated or unsaturated alkyl chain, for instance guar gum alkylated with C_1 to C_6, and in particular C_1 to C_3, alkyl chains, and mixtures thereof. The "diblock" or "triblock" type block copolymers of the polystyrene/polyisoprene or polystyrene/polybutadiene type such as those sold under the name "Luvitol HSB®" by the company BASF, of the polystyrene/copoly(ethylene-propylene) type such as those sold under the name "Kraton®" by the company Shell Chemical Co or of the polystyrene/

copoly(ethylene-butylene) type.

Among the lipophilic gelling agents which may be used in the compositions according to the invention, mention may also be made of fatty acid esters of dextrin such as dextrin palmitates, especially such as those sold under the names "Rheopearl TL®" or "Rheopearl KL®" by the company Chiba Flour.

Needless to say, a person skilled in the art will take care to select the optional additional additives and/or the amount thereof such that the advantageous properties of the composition according to the invention are not, or are not substantially, adversely affected by the addition envisaged.

The composition according to the invention may be manufactured by known processes generally used in the cosmetic field.

Preferably, the composition according to the invention is a mascara.

The composition according to the invention may be packaged in a cosmetic set comprising a container delimiting at least one compartment which comprises the said composition, the said container being closed by a closing member.

The container is preferably combined with an applicator, especially in the form of a brush comprising an arrangement of bristles maintained by a twisted wire. Such a twisted brush is described

especially in patent US 4 887 622. It may also be in the form of a comb comprising a plurality of application members, obtained especially by moulding. Such combs are described for example in patent FR 2 796 529. The applicator may be integrally attached to the container, as described for example in patent FR 2 761 959. Advantageously, the applicator is integrally attached to a rod which is itself integrally attached to the closing member.

The closing member may be coupled to the container by screwing. Alternatively, the coupling between the closing member and the container is done other than by screwing, especially via a bayonet mechanism, by click-fastening or by tightening. The term "click-fastening" in particular means any system involving the crossing of a bead or cord of material by elastic deformation of a portion, especially the closing member, followed by return to the elastically unconstrained position of the said portion after the crossing of the bead or cord.

The container may be at least partially made of thermoplastic material. Examples of thermoplastic materials that may be mentioned include polypropylene or polyethylene.

Alternatively, the container is made of non thermoplastic material, especially glass or metal (or alloy).

The container is preferably equipped with a drainer arranged in the region of the aperture of the container. Such a drainer makes it possible to wipe the applicator and possibly the rod to which it may be integrally attached. Such a drainer is described for example in patent FR 2 792 618.

The content of the patents or patent applications cited above are incorporated by reference into the present application.

The invention is illustrated in greater detail in the following examples.

The quantities are given in grams.

Example 1: Preparation of a poly(isobornyl acrylate/ isobutyl methacrylate/2-ethylhexyl acrylate) polymer

100 g of isododecane are introduced into a 1 litre reactor, and then the temperature is increased so as to pass from room temperature (25°C) to 90°C in 1 hour.

120 g of isobornyl acrylate, 90 g of isobutyl methacrylate, 110 g of isododecane and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox® 141 from Akzo Nobel) are then added at 90°C and over 1 hour.

The mixture is maintained for 1 h 30 min at 90°C.

90 g of 2-ethylhexyl acrylate, 90 g of isododecane and 1.2 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-

dimethylhexane are then introduced into the preceding mixture, still at 90°C and over 30 minutes.

The mixture is maintained for 3 hours at 90°C, and then the whole is cooled.

A solution containing 50% polymer active material in isododecane is obtained.

A polymer comprising a poly(isobornyl acrylate/isobutyl methacrylate) first block with a Tg of 80°C, a poly(2-ethylhexyl acrylate) second block with a Tg of -70°C and an intermediate block which is an isobornyl acrylate/isobutyl methacrylate/ 2-ethylhexyl acrylate random polymer is obtained.

This polymer has a weight-average mass of 77 000 g/Mol and a number-average mass of 19 000, i.e. a polydispersity index I of 4.05.

Example 2: Preparation of a poly(isobornyl acrylate/ isobornyl methacrylate/2-ethylhexyl acrylate) polymer

100 g of isododecane are introduced into a 1 litre reactor, and then the temperature is increased so as to pass from room temperature (25°C) to 90°C in 1 hour.

105 g of isobornyl acrylate, 105 g of isobornyl methacrylate, 110 g of isododecane and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox® 141 from Akzo Nobel) are then added at 90°C and over 1 hour.

The mixture is maintained for 1 h 30 min at

90°C.

90 g of 2-ethylhexyl acrylate, 90 g of isododecane and 1.2 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane are then introduced into the preceding mixture, still at 90°C and over 30 minutes.

The mixture is maintained for 3 hours at 90°C, and then the whole is cooled.

A solution containing 50% polymer active material in isododecane is obtained.

A polymer comprising a poly(isobornyl acrylate/isobornyl methacrylate) first block with a Tg of 110°C, a poly(2-ethylhexyl acrylate) second block with a Tg of -70°C and an intermediate block which is an isobornyl acrylate/isobornyl methacrylate/2-ethylhexyl acrylate random polymer is obtained.

This polymer has a weight-average mass of 103 900 g/Mol and a number-average mass of 21 300, i.e. a polydispersity index I of 4.89.

Example 3: Preparation of a poly(isobornyl methacrylate/isobutyl methacrylate/isobutyl acrylate) polymer

100 g of isododecane are introduced into a 1 litre reactor, and then the temperature is increased so as to pass from room temperature (25°C) to 90°C in 1 hour.

120 g of isobornyl methacrylate, 90 g of isobutyl methacrylate, 110 g of isododecane and 1.8 g

of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox® 141 from Akzo Nobel) are then added at 90°C and over 1 hour.

The mixture is maintained for 1 h 30 min at 90°C.

90 g of isobutyl acrylate, 90 g of isododecane and 1.2 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane are then introduced into the preceding mixture, still at 90°C and over 30 minutes.

The mixture is maintained for 3 hours at 90°C, and then the whole is cooled.

A solution containing 50% polymer active material in isododecane is obtained.

A polymer comprising a poly(isobornyl methacrylate/isobutyl methacrylate) first block with a Tg of 95°C, a poly(isobutyl acrylate) second block with a Tg of -20°C and an intermediate block which is an isobornyl methacrylate/isobutyl methacrylate/isobutyl acrylate random polymer is obtained.

This polymer has a weight-average mass of 100 700 g/Mol and a number-average mass of 20 800, i.e. a polydispersity index I of 4.85.

Example 4: Preparation of a poly(isobornyl acrylate/ isobutyl methacrylate/isobutyl acrylate) polymer

100 g of isododecane are introduced into a 1 litre reactor, and then the temperature is increased so as to pass from room temperature (25°C) to 90°C in

1 hour.

120 g of isobornyl acrylate, 90 g of isobutyl methacrylate, 110 g of isododecane and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox® 141 from Akzo Nobel) are then added at 90°C and over 1 hour.

The mixture is maintained for 1 h 30 min at 90°C.

90 g of isobutyl acrylate, 90 g of isododecane and 1.2 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane are then introduced into the preceding mixture, still at 90°C and over 30 minutes.

The mixture is maintained for 3 hours at 90°C, and then the whole is cooled.

A solution containing 50% polymer active material in isododecane is obtained.

A polymer comprising a poly(isobornyl acrylate/isobutyl methacrylate) first block with a Tg of 75°C, a poly(isobutyl acrylate) second block with a Tg of -20°C and an intermediate block which is an isobornyl acrylate/isobutyl methacrylate/ isobutyl acrylate random polymer is obtained.

This polymer has a weight-average mass of 144 200 g/Mol and a number-average mass of 49 300, i.e. a polydispersity index I of 2.93.

The following polymer may be prepared.

Example 5: Preparation of a poly(isobornyl

acrylate/isobutyl methacrylate/2-ethylhexyl acrylate) polymer

100 g of isododecane are introduced into a 1 litre reactor, and then the temperature is increased so as to pass from room temperature (25°C) to 90°C in 1 hour.

54 g of isobornyl acrylate, 75.6 g of isobutyl methacrylate, 50.4 g of 2-ethylhexyl acrylate, 110 g of isododecane and 1.8 g of 2,5-bis(2-ethyl-hexanoylperoxy)-2,5-dimethylhexane (Trigonox® 141 from Akzo Nobel) are then added at 90°C and over 1 hour.

The mixture is maintained for 1 h 30 min at 90°C.

120 g of 2-ethylhexyl acrylate, 90 g of isododecane and 1.2 g of 2,5-bis(2-ethylhexanoyl-peroxy)-2,5-dimethylhexane are then introduced into the preceding mixture, still at 90°C and over 1 hour.

The mixture is maintained for 3 hours at 90°C, and then the whole is cooled.

A solution containing 50% polymer active material in isododecane is obtained.

A polymer comprising a poly(isobornyl acrylate/isobutyl methacrylate/2-ethylhexyl acrylate) first block with a Tg of 25°C, a poly(2-ethylhexyl acrylate) second block with a Tg of -50°C and an intermediate block which is an isobornyl acrylate/ isobutyl methacrylate/2-ethylhexyl acrylate random

polymer is obtained.

Examples 6 to 10: Waterproof mascaras

The following mascara compositions 9 and 10 according to the invention and 6 to 8 according to the prior art were prepared:

	Example				
	6	**7**	**8**	**9**	**10**
Paraffin wax	15	10		5	5
Beeswax	5	10		5	5
Block polymer of Example 1 as active material (a.m.)	10	10		25	-
Block polymer of Example 3 as a.m.				-	25
Modified hectorite ("Bentone 38V®" from Elementis	5.32				
Propylene carbonate	1.74				
Rice starch	0.8				
Pigment	8				

For each composition, the dry extract was measured according to the method of measurement described above in the description.

The staying power of the film formed by the composition according to the invention is evaluated by measuring the water resistance, as a function of time, of a film of composition spread onto a glass plate and subjected to stirring in aqueous medium. The protocol is as follows:

At ambient temperature (25°C), a layer of composition 300 µm thick (before drying) with a surface area of 9 cm × 9 cm is spread onto a glass plate with a surface area of 10 cm × 10 cm, and is then left to dry for 24 hours at 30°C and 50% relative humidity. After drying, the plate is placed in a 2 litre crystallizing dish 19 cm in diameter, filled with 1 litre of water and placed on a heating magnetic stirrer sold under the name RCT basic by the company IKA Labortechnik. A smooth cylindrical PTFE magnetic bar (6 cm long; 1 cm diameter) is then placed on the film. The stirring speed is set to position 5. The water temperature is controlled using a thermometer to a temperature of 20°C or 40°C. At time $t_0 = 0$, the stirring is started. The time t (expressed in minutes) after which the film begins to detach or debond from the plate or when a hole the size of the stirring magnetic bar is observed, i.e. when the hole has a diameter of 6 cm, is measured. The water resistance of the film corresponds to the time t measured.

The measurement of the viscosity is carried out using the Rheomat RM 180 equipped with a spindle MS-r3 or Ms-r4 revolving at 240 min^{-1} for a current supply at 60 Hz or at 200 min^{-1} for a current supply at 50 Hz.

	Example				
	6	**7**	**8**	**9**	**10**
Viscosity	Not			7.6	17.5

Dry extract %	measurable, too thick	51	51
Staying power (crystallizing dish test		Greater than 1 day	Greater than 1 day

These mascara compositions according to the invention are easy to apply to the eyelashes. The mascara forms a smooth and homogeneous makeup, and thickens the eyelashes. It exhibits a very good staying power.

Examples 11 and 12

A mascara comprising a block polymer according to the invention (Example 12) and a mascara not forming part of the invention (Example 11) having the following composition were prepared:

	Example 11 (comparative)	**Example 12 (according to the invention)**
Carnauba wax	4.7	4.7
Beeswax	8.2	8.2
Rice bran wax	2.2	2.2
Modified hectorite ("Bentone 38V®" from Elementis	5.5	5.5
Paraffin wax	2.2	2.2
Talc	1	1
Vinyl acetate/allyl stearate copolymer (Mexomère PQ from the company Chimex)	6.7	6.7
Block polymer of Example 1	-	10
Polyvinyl laurate	0.7	0.7

(Mexomère PP from the company Chimex)		
Sulphopolyester (Eastmann AQ 55S from Eastmann)	0.1	0.1
Preservatives	0.2	0.2
Propylene carbonate	1.8	1.8
Water	7	7
Pigments	5.2	
Isododecane	qs 100	qs 100

For each composition, the dry extract and the staying power were measured according to the methods of measurement described above in the description.

The charge in vitro is measured by gravimetry on test pieces of Caucasian curly hair (30 hair strands 1 cm long distributed over a distance of 1 cm).

The test piece is made up by carrying out 3 × 10 passages of mascara separated by 2 minutes with taking up of the product between each series of 10.

The test piece is dried for 10 min at ambient temperature and then weighed.

This measurement is carried out on 6 test pieces.

The charge is in fact the quantity of material deposited on the test piece = made up test piece mass - bare test piece mass.

The mean charge is the mean of the measurements carried out on the 6 test pieces.

The results below were obtained.

	Example 11	**Example 12**
Viscosity (in Pa.s)	5.4	4
Dry extract measured (%)	35.3	45.4
Charge in vitro (Mg)	4.9 ± 0.7	8.9 ± 0.9
Staying power (crystallizing dish test)	About 1 hour	Greater than 1 day

It is observed that the mascara of Example 12 according to the invention has a charge in vitro and a dry extract and a staying power greater than the mascara and not comprising a block polymer (Example 11), while having a low viscosity.

The mascara is easy to apply to the eyelashes and exhibits, after application, a charging effect on the eyelashes, while having good staying power.

Examples 13 to 16

Mascaras comprising a block polymer according to the invention (Examples 14 to 16) and a mascara not forming part of the invention (Example 13) having the following composition were prepared:

	Example 13 (comparative)	**Example 14 (according to the invention)**	**Example 15 (according to the invention)**	**Example 16 (according to the invention)**
Paraffin wax	2.3	2.3	2.3	2.3
Carnauba wax	6.6	6.6	6.6	6.6
Polyolefin wax	2.1	2.1	2.1	2.1
Beeswax	8.3	8.3	8.3	8.3
Modified hectorite	5.8	5.8	5.8	5.8
Siliconized candelilla wax	1	1	1	1
Rice starch	1.5	1.5	1.5	1.5

Vinylpyrrolidone/ eicosene copolymer	2	2	2	2
Vinyl acetate/ allyl stearate copolymer (Mexomère PQ from the company Chimex)	2.7	2.7	2.7	2.7
Block polymer of Example 3 (as AM)	-	10		
Block polymer of Example 4 (as AM)			10	
Block polymer of Example 1 (as AM)				10
Polyvinyl laurate	0.7	0.7	0.7	0.7
Preservatives	0.1	0.1	0.1	0.1
Polybutene	1	1	1	1
Propylene carbonate	1.9	1.9	1.9	1.9
Water	7.6	7.6	7.6	7.6
Ethanol	2.7	2.7	2.7	2.7
Black iron oxide	4.2	4.2	4.2	4.2
Isododecane	qs 100	qs 100	qs 100	qs 100

For each composition, the dry extract was measured according to the method of measurement described above in the description.

The charge in vitro and the staying power were measured according to the method described in the preceding examples.

The results below were obtained

	Example 13	Example 14	Example 15	Example 16
Dry extract measured (%)	38.1	47.8	48.3	49.7
Charge in vitro (Mg)	6.2 ± 1	8.4 ± 1.4	7.8 ± 0.7	7.8 ± 0.9
Staying power	About 15 min	Greater than 1 day	Greater than 1 day	About 16 hours

It is observed that the mascaras of Examples 14 to 16 according to the invention have a staying power greater than the mascara not comprising a block polymer (Example 13), and a greater charge in vitro.

Examples 17 to 19: Wax-free mascaras

The following mascaras according to the invention were prepared:

	Example 17	Example 18	Example 19
Block polymer of Example 1 (as AM)	-	-	45
Block polymer of Example 3 (as AM)	45	45	-
Mixture of butylene/ethylene/ styrene triblock copolymer and ethylene/propylene/styrene starburst copolymer in isododecane (Versagel MD 960 from the company Penreco)	-	-	-
Octyldodecanol	-	0.6	-
Parleam oil	-	1.4	-
Phenyl trimethicone (DC556 from Dow Corning)	-	1.4	-
PVP eicosene	-	3.3	-
Pigment	10	3.3	10

For each composition, the dry extract was measured according to the method of measurement described above in the description.

The average gloss of these compositions was also measured according to the following protocol:

A layer of between 50 µm and 150 µm thick of the composition is spread on a contrast card of Leneta trade mark and having the reference Form 1A Penopac with the aid of an automated spreading machine. The layer covers at least the white base of the card. The deposit is allowed to dry for 24 hours at a temperature of 30°C, and then the gloss is measured at 60° on the white base with the aid of a glossmeter of Byk Gardner trade mark and having the reference microTri-Gloss.

This measurement (between 0 and 100) is repeated at least three times, and the average gloss is the average of the at least three measurements performed.

The following results are obtained:

	Example 17	**Example 18**	**Example 19**
Dry extract	58.2	54.6	55
Crystallizing dish staying power	Greater than 1 day	Greater than 1 day	Greater than 1 day
Average gloss	71.9	81.8	82.5

These mascaras exhibit good staying power. It is also observed that the gloss value of the composition increases with the level of block polymer.

Example 20

1) The average gloss of the mascara of Example 13 according to the prior art is measured using the protocol described above.

2) A film of mascara composition of Example 13 (base coat) 300 micrometres thick is spread on a glass plate.

It is allowed to dry for 2 hours at ambient temperature (25°C).

A film of the composition of Example 18 (top coat) 300 micrometres thick is then spread on the film of the composition of Example 13.

The whole is allowed to dry for 24 hours at ambient temperature (25°C).

The average gloss and the staying power of the final film are then measured according to the protocols described above.

3) The results are presented in the following table:

	Example 13	**Example 13 (base coat) + Example 18 (top coat)**
Average gloss	1.7	60.4
Staying power	15′	1 day

The application of the mascara of Example 18 according to the invention as top coat over the mascara of Example 13 according to the prior art makes it possible to obtain a film of composition exhibiting a gloss and a staying power which are greater than those of the base mascara film alone.

Examples 21 to 24

The compositions of Examples 22 to 24

comprising a block polymer according to the invention and the composition of Example 21 (comparative) not comprising a block polymer were prepared.

<table>
<tr><th></th><th>Example 21 (comparative)</th><th>Example 22 (according to the invention)</th><th>Example 23 (according to the invention)</th><th>Example 24 (according to the invention)</th></tr>
<tr><td>Candelilla wax</td><td>20</td><td>20</td><td>15</td><td>5</td></tr>
<tr><td>Beeswax</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Paraffin wax</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Carnauba wax</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Block polymer of Example 4</td><td>-</td><td>5</td><td>10</td><td>20</td></tr>
<tr><td>Stearic acid</td><td colspan="4">5.8</td></tr>
<tr><td>Triethanolamine stearate</td><td colspan="4">2.9</td></tr>
<tr><td>Black iron oxide</td><td colspan="4">8</td></tr>
<tr><td>Hydroxyethyl-cellulose</td><td colspan="4">0.9</td></tr>
<tr><td>Gum arabic</td><td colspan="4">3.4</td></tr>
<tr><td>Water, preservatives</td><td colspan="4">qs 100</td></tr>
</table>

For each composition, the dry extract was measured according to the method of measurement described above in the description.

The charge in vitro was measured according to the method described in the preceding examples.

The following results are obtained:

	Example 21	Example 22	Example 23	Example 24
DE measured (%)	38.8	45.25	45.89	45.12
Charge in vitro (mg)	6.73 ± 0.64	8.98 ± 1.24	8.68 ± 1.30	9.13 ± 1.43
Staying power	55""	1'25"	1'40"	2'18"

The mascaras according to the invention comprising the specific block polymer have a dry extract of greater than or equal to 45% and a high charge value in vitro while being easy to apply.

After application to the eyelashes, the composition film additionally exhibits good resistance to crumbling and to sebum, while being easy to remove when used as makeup using a conventional makeup remover.

Example 25

The following mascara is prepared:

Candelilla wax	5 g
Ethyl acrylate/methyl methacrylate copolymer; (80/20) as an aqueous dispersion at 50% AM ("Daitosol 5000 AD®" from Daito	10 (AM)
Block polymer of Example 4	10 (AM)
Stearic acid	5.8
Triethanolamine stearate	2.9
Black iron oxide	8
Hydroxyethylcellulose	0.9
Gum arabic	3.4
Water, preservatives	qs 100

The dry extract and the staying power were measured according to the methods of measurement described above in the description.

The results obtained are presented in the following table:

DE measured (%)	45.2
Charge in vitro (mg)	12.5 ± 1.42
Staying power	2′24″

This mascara exhibits good staying power and a thickening making up of the eyelashes.